Electro-chemical manifestation of nanoplasmonics in fractal media

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Abstract

Electrodynamics of composite materials with fractal geometry is studied in the framework of fractional calculus. This consideration establishes a link between fractal geometry of the media and fractional integro-differentiation. The photoconductivity in the vicinity of the electrode-electrolyte fractal interface is studied. The methods of fractional calculus are employed to obtain an analytical expression for the giant local enhancement of the optical electric field inside the fractal composite structure at the condition of the surface plasmon excitation. This approach makes it possible to explain experimental data on photoconductivity in the nano-electrochemistry.

KEYWORDS: fractals fractional integro-differentiation electrochemical potential

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1 Introduction

It is well known that small-particle composites, like nano-structured noble-metal-dielectric composites, establishes a striking response to the electromagnetic irradiation [1, 2, 3]. This effect differs radically from one taking place in both ordinary bulk materials or individual nanoparticles. We are speaking about so-called hot spots, which result from strong localization of optical energy on the nanometer scale (less than the optical wavelength). This effect is inherent in disordered clusters of nano-particles at the condition of the surface plasmon excitation.

This effect has a more pronounced manifestation on fractal clusters. Fractals are not translationally invariant systems (as any disordered systems), and, therefore, can not transmit running waves [4]. As a result, dynamical excitations, like surface plasmons, tend to be localized in fractals. Note, that a superposition of electric fields induced by local surface plasmons results in focusing and local giant enhancement of the electric field. This giant enhancement has a geometrical nature of the scale invariance of fractals, which, at some extend, has the the same nature as X-ray diffractive maxima are the geometrical effect of a spatial periodicity of crystals.

In this paper we employ a concept of fractals and fractional calculus for application to the electrolysis enhancement in nano-electrochemistry. An enhancement of the electrolysis current

due to a rough metal-electrode interface was first observed in 1926 [5]. The further enhancement can be also observed when the electrolysis set up is extend to the light electromagnetic field [6, 7, 8]. This optical induced current is due interplay between the light and fractional nanostructure which is the double electric layer on the fractal electrode interface. This leads to a local giant enhancement of electric field. Technically, these "hot spots" lead to the breakdown of the double layer capacitor that, eventually, changes the electrode potential (potential of the Stern layer). The hot spot phenomenon is well known in optics, and relates to optical properties of metal nanoparticles, and is largely due to their ability to produce giant and highly localized electromagnetic fields. Two phenomena, closely related to each other, are responsible for giant enhancement. The first one is localized surface plasmon resonance (see, for examples the reviews [3, 2], or monograph [1]), which is charge density oscillations confined to conducting (metallic) nanostructures. Strong enhancement of the electromagnetic field is possible if its frequency is near the frequency of these oscillations [1, 2, 9, 10, 11]. Another giant enhancement due to fractal geometry is a so-called geometrical enhancement [12], obtained analytically in the framework of fractional calculus, where a question of its experimental manifestation is still open [13] .

Application of fractional integro-differentiation and its link to fractals and fractal geometry may shed a new light on studies of properties of composite materials with underlying fractal structures [14, 15, 16, 17]. The fractal concept makes it possible to involve the application of the powerful methods of fractional integro-differentiation, see *e.g.*, [18, 19]. Extended reviews on fractional calculus can be found in [18, 19, 20], and a brief survey is presented in Appendix A.

In this paper, we suggest an analytical consideration, based on fractional calculus, for the purpose of obtaining an analytical expression for the electric field in fractal composite media, namely in fractal electrode-electrolyte interface. This approach establishes a relation between the fractal geometry of the medium and fractional integro-differentiation, and it is also based on our previous studies [12, 22, 21]. We suggest a coarse graining procedure for the electric field in the Maxwell equation to treat the electric induction term, which is a discontinuous function in the fractional composite media. This smoothing procedure makes it possible to involve the fractional calculus in (quasi-)continuous media [23] and, in the present particular case, to obtain an equation for the electric field in a closed form including the fractal polarization charge distribution. The main idea is due a seminal result [24], where a link between fractal geometry and fractional integro-differentiation is constituted in the procedure of averaging an extensive physical value. It should be admitted that this description of properties of fractal media in the framework of the fractional calculus is possible only in some approximation. This procedure of filtering, expressed by means of a smooth function over a Cantor set, leads to fractional integration. In its eventual form, it has been presented in Ref. [25]. This topics was extensively studied [23, 24] in application for signal processing and dielectric relaxation in complex media [26, 27, 28].

The main idea of filtering, or embedding a matter inside a fractal is the construction of a convolution integral according integration over the fractal volume $\mu(x) \sim x^{\alpha}$

$$\langle F(x) \rangle = \int F(x) d\mu(x) \Rightarrow {}_0I_x^{\alpha} F(x) \,, \tag{1}$$

where ${}_0I_x^\alpha$ designates the fractional integral of the order of α in the range from 0 to x:

$$ {}_0I_x^\alpha F(x) = \frac{1}{\Gamma(\alpha)} \int_0^x (x-x')^{\alpha-1} F(x') dx' \,. \tag{2}$$

Here $\Gamma(\alpha)$ is a gamma function and α is the fractal dimension. For example, in Ref. [25] this kind of integration has been obtained by means of averaging over one of a parameter, which describes a fractal structure. Considering a convolution integral $F(x) = W(x) \star f(x) = \int_0^x W(x-y) f(y) dy$ with the function $W(x)$, which obeys the scaling relation $W(x) = \frac{1}{a} W(bx)$ and describes a Cantor set, one performs averaging over the parameter b (namely $\ln b$ [25]) and obtains Eq. (1), where the averaging reads $\langle F(x) \rangle_{\ln b} = A(\alpha, b) {}_0I_x^\alpha f(x)$, where $A(\alpha, b)$ is a constant factor and $\alpha = \frac{\ln a}{\ln b}$. Instead parameters a and b one introduces the fractal dimension α and the log-periodicity parameter $\ln b$. Therefore, averaging over the log-periodicity means averaging over the all possible realizations of the fractal.

It should be stressed that this idea was firstly expressed by Kolmogorov in [29] for fractional Brownian motion, and later rediscovered by Mandelbrot and Van Ness, who explored this phenomenon in greater detail in [30].

As shown [12, 21, 22], these mathematical constructions are also relevant to the study of electrostatics of real composite structures. The main objective of the present research is to solve a standard electrostatic problem, namely, the derivation of the electric field in a fractal metal-dielectric composite on the electrode-electrolyte interface in the presence of the double layer capacitor. This leads to the exploration of the fractional Maxwell equations. This issue attracts much attention and is also extensively studied to explore the role of fractional calculus in electrodynamics [31, 32, 33, 34, 35] (see review [36]).

This formulation can be also employed for the fractal geometry, in particular, for the exploration of the electric field in fractal dielectric composites [37, 21], or metal–dielectric composites [12, 21]. This problem is important for nanoplasmonics, where the interplay between the light and fractional nanostructures leads to a local giant enhancement of the electric field [1, 2].

2 Electro-mechanical consideration of electron motion in the double layer

The double layer plays a central role for stability in electrolysis current phenomenon near the electrodes, see, for example, [38]. An electron motion inside the double layer in the presence of the external high-frequency electric field is described by equation

$$ m\ddot{x} = -\frac{dU}{dx} + f(\omega t) \,. \tag{3}$$

Here $U(x)$ is the double layer constant field potential, which is considered as a capacitor potential, while $f(\omega t) = f_0 \cos \omega t = eE_0(t)$ is a fast-oscillating perturbation, such that $\omega \mathcal{T} \gg 1$, where $\mathcal{T}$ is an averaged time propagation through the double layer. Here $E_0(t)$ is the electric component of the external light and e the electron charge. It is well known that the average procedure over the fast oscillations leads to the additional term to the potential due to the kinetic term [39]

$$ U_{\text{eff}} = U + \frac{f_0^2}{4m\omega^2} = U + U_f \,. \tag{4}$$

This additional term leads, eventually, to effective decrease of the double layer capacitor potential $W \to We^{-\frac{U_f}{kT}}$, where k_BT is the Boltzman temperature. To show this let us consider the Poisson-Boltzmann theory of the diffusive double layer [38].

2.1 The Poisson-Boltzmann equation

Now we follow the Poisson-Boltzmann theory near the double layer [38]. For the considered planar surface, the x coordinate determines the direction of the potential change in the double layer. Therefore, the electric potential $\psi(x)$ near a charged planar electrode interface with the surface potential $\psi(x=0)=\psi_0$, taken as the boundary condition for the double layer, is determined by the one-dimensional Poisson equation

$$\frac{d^2\psi(x)}{d\,x^2} = -\frac{\rho(x)}{\varepsilon_d}\,, \tag{5}$$

where $\rho(x)$ is the local electric charge density and ε_d is the permittivity of dielectric solution (at this point it does not carry any important information). The charge density is determined by the Boltzmann statistics that reads for the local ion density $n_i = n_0 e^{-A_i/k_BT}$, where A_i is the performed work to bring an ion from infinity to the point x inside the double layer. In the presence of the additional potential term U_f in (4) due to breakdown of the double layer capacitor, the electric work A_i depends on the ion charge. Namely, to bring cation the required work is $A_- - U_f = -e\psi(x)$, while for anion it is $A_+ + U_f = e\psi$. Therefore, the effective potential decreases, and since U_f is independent of the coordinates x, this leads to only to re-scaling of the boundary condition $psi_0 \to \psi_0 - U_f/e$. This leads to change of the constant value of the solution of the Poisson-Boltzman equation (5) $\psi(x) = (\psi_0 - U_f/e)\Psi(x)$, where $\Psi(x=0)=1$.

To see this effect of the external light influence on the electrolysis, one needs $U_f \sim k_BT$. If the electric component of the external light, with $\omega \sim 10^{15}$, is $E_0 \sim 1 \div 10\, V/cm$, the additional potential energy is $U_f \sim (10^{-9} \div 10^{-7}) k_BT$, which is vanishingly smaller than temperature fluctuations. Therefore, a condition of observation this effect of the influence of the external light on the electrode potential is an essential enhancement of the electric field of the order of $10^5 \div 10^6$ times due to the surface plasmon resonance that yields the respond/enhanced electric field of the order of $10^6 \div 10^7$(V/cm). Effect of this giant enhancement of the external low-intensity light is considered in the quasi-static approximation.

3 Quasi-static Electromagnetic Field

The fractal nanostructure placed on the electrode surface is embedded in the $3D$ space, therefore, we consider a sample of a size R which consists of a fractal metal nanosystem embedded in a dielectric (electrolyte) host medium. The system is subject to an external electromagnetic field $\mathbf{E}_0(t)$ at an optical frequency ω, and in the experimental setup, the double layer fractal-host inhomogeneities (of the order of R) are much smaller than the light wavelength λ. In this case, a quasi-static approximation is valid [40]. Therefore, the nanosystem contains a metallic fractal with a fractal volume $V_D \sim R^D$ and the permittivity $\varepsilon_m(\omega)$, which depends on optical frequency ω, while the dielectric-electrolyte host has the volume V_h and the permittivity ε_d. At the considered scale, the magnetic component is not important and cannot be considered. The

electric component satisfies the Maxwell equation in the Fourier frequency domain

$$\nabla \cdot \Big[\varepsilon(\mathbf{r},\omega)\mathbf{E}(\mathbf{r},\omega)\Big] = 0\,. \tag{6}$$

The permittivity can be expressed by means of a characteristic function $\chi(\mathbf{r})$ [11, 41, 12] in the form $\varepsilon(\mathbf{r},\omega) = \varepsilon_m(\omega)\chi(\mathbf{r}) + \varepsilon_d[1-\chi(\mathbf{r})]$, where the characteristic function inside the fractal is $\chi(\mathbf{r}) = 1$, $\mathbf{r}(x,y,z) \in V_D$, while inside the dielectric host it reads $\chi(\mathbf{r}) = 0$, $\mathbf{r}(x,y,z) \in V_h$. Following Ref. [12], one splits the electric field into the two components $\mathbf{E}(\mathbf{r}) = \tilde{\mathbf{E}}(\mathbf{r}) + \mathbf{E}_1(\mathbf{r})$ and looks for the reaction of the nanosystem on the external field, where $\tilde{\mathbf{E}}(\mathbf{r})$ is the electric field induced by $\mathbf{E}_0$ in the homogeneous nanosystem, when $\chi(\mathbf{r}) = 0$ for $\forall\ \mathbf{r}$, or $\chi(\mathbf{r}) = 1$ for $\forall\ \mathbf{r}$ and $\nabla\tilde{\mathbf{E}}(\mathbf{r}) = 0$. Here $\mathbf{E}_1(\mathbf{r})$ results from inhomogeneity of the nanostructute. Thus Eq. (6) can be rewritten in the form

$$\chi(\mathbf{r})\nabla\cdot\mathbf{E}_1(\mathbf{r}) - q(\omega)\nabla\cdot\mathbf{E}_1(\mathbf{r}) + \mathbf{E}_1(\mathbf{r})\cdot\nabla\chi(\mathbf{r}) = -\tilde{\mathbf{E}}(\mathbf{r})\cdot\nabla\chi(\mathbf{r})\,, \tag{7}$$

where $q(\omega) = \frac{\varepsilon_d}{\varepsilon_d - \varepsilon_m(\omega)}$. In general case, mixed (Dirichlet, or Neumann) boundary conditions are imposed [11, 41]. It follows from the boundary conditions that $\nabla\cdot\mathbf{E}(\mathbf{r},\omega) = 0$ with $\mathbf{E}(\mathbf{r}\in S,\omega) = \mathbf{E}_0(\omega)$, where S means boundaries. This also supposes $\chi(\mathbf{r}\in S) = 0$.

3.1 Filtering inside a random fractal

Since the characteristic function $\chi(\mathbf{r})$ is discontinuous, the next step of our consideration is coarse-graining the electric field, which is averaging Maxwell's Eq. (7). This procedure relates to integration with the characteristic function $\int\chi(\mathbf{r})\nabla\mathbf{E}_1(\mathbf{r})dV$ and evaluation of the integral of the polarization charge density term $\int\nabla\chi(\mathbf{r})\cdot\mathbf{E}(\mathbf{r})dV$. To that end, let us consider a spherical volume of the radius r, such that $l_0 \ll r < R$, where l_0 is a minimal size of the self-similarity of the fractal volume on the electrode corrugated/fractal surface. In the sequel we will work with dimensionless variable $r/l_0 \to r$. The electric field does not change at this scaling. A fractal mass inside the volume is $\mathcal{M}(r) \sim r^D$, where $0 < D < 3$. Therefore, an average density of the metallic phase is of the order of r^{D-3}. For the filtering mass inside the fractal, we consider convolution in Eqs. (1) and (2). We also, reasonably, suppose that the random fractal composite is isotropic, *i.e.*, the (averaged) similarity exponents coincides along all directions. This yields that one takes into account only radius r and any changes in the inclination and azimuth angle directions can be neglected (this means that the averaged fractal aggregate is considered as a sphere with a radially dependent filling factor r^D). Then, we have for the divergence

$$\nabla\cdot\mathbf{E}_1(\mathbf{r}) = \nabla_r E_{r,1}(r) \equiv \nabla_r E_1(r)\,. \tag{8}$$

Using property of the characteristic function, we obtain that the measure of the fractal volume V_D is $\mu(V_D) = \int\chi(V_D)dV = \int\rho dV_D$, where $dV_D = \frac{2^{3-D}\Gamma(3/2)}{\Gamma(D/2)}|\mathbf{r}|^{D-3}r^2dr\sin\theta d\theta d\phi$ is the elementary fractional volume in the spherical coordinates and ρ is a fractal density factor. In what follows, we will use $\mu(r)$ as the fractal volume by means of the fractal density $\sum_{r_j\in V_D}\delta(r'-r_j)$ and for simplicity, violate all constants. Therefore, the fractal volume reads

$$\mu(r) = r^D = \int_0^r \sum_{r_j\in V_D}\delta(r'-r_j)r'^2dr'\,. \tag{9}$$

Now, filtering inside the fractal due to characteristic function, which depends only on the radius r, yields the integrations

$$\frac{1}{4\pi}\int \chi(\mathbf{r})\nabla_r E_1(r)dV = \int_0^r \chi(r')[\nabla_r E_1(r')]r'^2 dr' = \int_0^r \sum_{r_j\in V_D} \delta(r'-r_j)G'(r')dr' \qquad (10)$$

Here we define $G(r) = r^2 E_1(r)$ and $G'(r) \equiv \frac{d}{dr}G$.

Following Ref. [42] (Theorem 3.1), we obtain

$$\int_0^r G'(r')d\mu(r') \sim \frac{1}{\Gamma(D-2)}\int_0^r (r-r')^{D-3}G'(r')dr' \equiv {}_0I_r^{D-2}G'(r)\,. \qquad (11)$$

Therefore, we consider the integration in Eq. (10) as the convolution integral with the averaged fractal density $(r-r')^{D-3}$.

Polarization term Now we estimate the integral $\int_0^r E(r')\nabla_{r'}\chi(r')r'^2dr'$. The fractal dust V_D at the Nth step of the construction consists of balls B_N with the radius Δ_N. For example, $\Delta_N \sim l_0$. In the limiting case one obtains $V_D = \lim_{N\to\infty}\bigcup B_N$ [43]. The characteristic function for every ball is $\chi(\Delta_N) = \Theta(r-r_j) - \Theta(r-r_j-\Delta_N)$. Differentiation of the characteristic function on the intervals $[r_j, r_j+\Delta_N]$ yields $\nabla_r\chi(\Delta_N) = \delta(r-r_j) - \delta(r-r_j-\Delta_N)$. Therefore, for any interval Δ_N and at $r = r_j$, integration with the electric field yields

$${}_rI^1_{r+\Delta_N}E(r)r^2\nabla_r\chi(r) = E(r)r^2 - E(r+\Delta_N)(r+\Delta_N)^2\,.$$

This expression is not zero in the limit $\Delta_N \to 0$. Let $E(r_j)$ is the electric field outside the ball B_N and $E(r_j+\Delta_N)$ denotes the internal electric field. The relation between them, due to Eq. (8.2) in Ref. [40] for polarization of a dielectric ball, is

$$E(r_j+\Delta_N) = \frac{3\varepsilon_d}{\varepsilon_m(\omega)+2\varepsilon_d}E(r_j)\,.$$

Therefore, the shift for the electric field in the limit $\Delta_N \to 0$ is

$$E(r_j) - E(r_j+0) = E(r_j)\frac{\varepsilon_m(\omega)-\varepsilon_d}{\varepsilon_m(\omega)+2\varepsilon_d}\,. \qquad (12)$$

Finally, integration of the polarization charge term yields

$$\int_0^r E(r')\nabla_{r'}\chi(r')r'^2dr' \equiv {}_0I_r^1E(r)r^2\nabla_r\chi(r) = \frac{\varepsilon_m(\omega)-\varepsilon_d}{\varepsilon_m(\omega)+2\varepsilon_d}\sum_{r_j\in V_D}\int_0^r E(r')r'^2\delta(r'-r_j)dr'\,. \qquad (13)$$

Again, one obtains the integration of the electric field with the fractal density $\mu(r') = \sum_{r_j\in V_D}\delta(r'-r_j)$. This corresponds to the fractal volume (9), and, hence, we consider the integration in Eq. (13) as the convolution integral of Eq. (11) with the averaged fractal density $(r-r')^{D-3}$. Note that this procedure is exactly corresponds to Nigmatulin's arguments on filtering according Eq. (1), where the convolution integral exists from the beginning, while in our case, the convolution integral appears owing to theorem of Ref. [42] for integration with the fractal volume/measure $\mu(r)$. Finally, commenting this procedure of filtering inside the fractal, it should be stressed

that integration with the fractal characteristic function in Eq. (10) leads to the integration with the fractal measure $\int \chi(r)G'(r)dr = \int G'(r)d\mu(r)$ that results from the physical properties of $\chi(r)$. On the contrary, integration with the differential $d\chi(r)$ in Eq. (13) leads again to the non-zero integration with the fractal measure $\int \chi'(r)G(r)dr = \int G(r)d\mu(r)$ due to the properties of the electric field, namely boundary properties of the electric field on the rough metal-electrode-electrolyte interface in the double layer capacitor.

Eventually, we obtain for the polarization charge term in Eq. (7)

$$\int_0^r E(r')\nabla_{r'}\chi(r')r'^2dr' \sim -\frac{p(\omega)}{\Gamma(D-2)}\int_0^r (r-r')^{D-3}E(r')r'^2dr' \equiv {}_0I_r^{D-2}[G(r)+\tilde{E}_0r^2]\,. \quad (14)$$

Here $\tilde{E}_0 = \tilde{\mathbf{E}}\cdot\hat{\mathbf{r}}$ is a projection of the external electric field on the radial direction inside the chosen spherical volume of the radius r and

$$p(\omega) = \frac{\varepsilon_d - \varepsilon_m(\omega)}{\varepsilon_m(\omega)+2\varepsilon_d}\,. \quad (15)$$

Taking all these arguments and results in Eqs. (11) and (14), one presents Eq. (7) in the coarse-graining form

$${}_0I_r^{D-2}G'(r) - q(\omega){}_0I_r^1G'(r) - p(\omega){}_0I_r^{D-2}G(r) = \frac{2p(\omega)\tilde{E}_0}{\Gamma(D+1)}r^D\,. \quad (16)$$

The Laplace transform can be applied to Eq. (16). Since $G(r=0) = G'(r=0) = 0$ (the electric field of fractal charge density diverges slowly than $\frac{1}{r^2}$ [12, 22, 34]), one obtains for $\tilde{G}(s) = \hat{\mathcal{L}}[G(r)]$ due to Eq. (26) (see Appendix):

$$\tilde{G}(s) = \frac{2p(\omega)\tilde{E}_0}{\varepsilon_d s^3}\cdot\frac{1}{s-q(\omega)s^{D-2}-p(\omega)}\,. \quad (17)$$

Note that the second term in Eq. (16) is $q(\omega)G(r)$.

Before arriving at the main result, let us consider the limiting cases. For $\varepsilon_m(\omega) = \varepsilon_d$ one obtains $q(\omega) = \infty$ and $p(\omega) = 0$. This yields $E_1(r) = 0$, and the solution for the electric field is $E(r) = \tilde{E}_0 \equiv \tilde{E}_r$. Another limiting case is $|\varepsilon_m(\omega)| \to \infty$. In this case $q(\omega) = 0$ and $p(\omega) = -1$, thus $E_1 \sim \tilde{E}_0$. Important result here is that permittivity of the mixture is approximately ε_d that corresponds to the well known result in Ref. [40] [see Eq. (9.7)].

4 Surface plasmon resonance

Now we consider a condition of the strong enhancement of the electric field at the surface plasmon resonance, when $Re[\varepsilon(\omega)] = -2\varepsilon_d$. This also known as the Fröhlich resonance [44, 45]. The permittivity of the metallic nanostructure inclusion at the resonance condition is a complex value $\varepsilon_m(\omega) = \varepsilon_1 + i\varepsilon_2$, where $\varepsilon_2/\varepsilon_1 \ll 1$ that is described by classical Drude formula (see *e.g.* [40, 45]) $\varepsilon_m(\omega) = \epsilon_0 - \frac{\omega_p^2}{\omega(\omega+i\gamma)}$, where ω_p is a so-called plasma frequency, ϵ_0 is a high-frequency lattice dielectric constant, while the attenuation coefficient γ is small in comparison with the resonant frequency. Therefore, we have for the metallic nanostructure $\varepsilon_m(\omega) = \varepsilon_1 + i\varepsilon_2$, where $\varepsilon_1 = \mathrm{Re}[\varepsilon_m(\omega)] = \epsilon_0 - \omega_p^2/\omega^2$ and $\varepsilon_2 = \mathrm{Im}[\varepsilon_m(\omega)] = \gamma\omega_p^2/\omega^3$.

At a small detuning from the resonance, when $Re[\varepsilon(\omega)] = -2\varepsilon_d + \varepsilon_2$ that corresponds to the width of the resonance in the frequency domain, $p(\omega)$ reaches the maximal values, that yields

$$p(\omega) = -1 + \frac{3\varepsilon_d}{2\varepsilon_2}(1-i) \approx \frac{3\varepsilon_d}{2\varepsilon_2}(1-i)\,, \tag{18}$$

$$q(\omega) = \frac{1}{3} - \frac{\varepsilon_2}{9\varepsilon_d}(1-i) \approx \frac{1}{3}\,. \tag{19}$$

These expressions are inserted in Eq. (17). Before carrying out the inverse Laplace transform $\hat{\mathcal{L}}^{-1}[\tilde{G}(s)]$, it is reasonable to simplify the second denominator. We recast Eq. (17) in the form

$$\tilde{G}(s) = 2p(\omega)\tilde{E}_0 \sum_{k=0}^{\infty} \frac{[q(\omega)s^{D-2} + p(\omega)]^k}{s^{k+4}}\,. \tag{20}$$

We take into account that for the scale $r \gg 1$, the Laplace parameter is small $s \ll 1$, and the binomial becomes approximately a monomial. The Laplace inversion of Eq. (20) can be performed using an expression for the Mittag-Leffler function [46]

$$\mathcal{E}_{(\nu,\beta)}(zr^{\nu}) = \frac{r^{1-\beta}}{2\pi i}\int_{\mathcal{C}} \frac{s^{\nu-\beta}e^{sr}}{s^{\nu}-z}ds = \frac{r^{1-\beta}}{2\pi}\int_{\mathcal{C}} e^{sr}\sum_{k=0}^{\infty}\frac{z^k}{s^{\nu k+\beta}}ds = \sum_{k=0}^{\infty}\frac{[zr^{\nu}]^k}{\Gamma(\nu k+\beta)}\,, \tag{21}$$

where $\mathcal{C}$ is a suitable contour of integration, starting and finishing at $-\infty$ and $\nu, \beta > 0$. Comparing Eqs. (20) and (21), $\beta = 4$ and $\nu = 1$, one obtains for the electric field

$$E_1(r) = 2p(\omega)\tilde{E}_0 r\mathcal{E}_{(1,4)}[p(\omega)r]\,. \tag{22}$$

Since the argument of the Mittag-Leffler function is large, its asymptotic behavior is [46]

$$E_1(r) \sim \frac{2\tilde{E}_0 r}{p^2(\omega)}e^{p(\omega)r} \propto \frac{\tilde{E}_0}{\varepsilon_d}\exp\left[r\frac{3\varepsilon_d}{2\varepsilon_2}(1-i)\right]\,. \tag{23}$$

Eventually, we arrived at the exponential (geometrical) enhancement and giant oscillations of the respond electric field due to the fractal geometry of the metal-dielectric composite.

4.1 Discussion on the geometrical enhancement of the electric field

As shown, the resulting (enhanced) electric field depends on the parameter $p(\omega)$, which is the pre-factor and the argument of the Mittag-Leffler function (when $r \sim 1$) in Eq. (22), and defined in Eq. (15). This parameter is absorbtion efficiency in the electrostatic (quasi-static) approximation [45]. In our case, it describes polarization, and it is obtained in Eq. (13) under evaluation of fractal boundary conditions. One should recognize that the linear (classical [45]) enhancement of the electric field is always takes place, due to Eq. (13) that corresponds to the enhancement of the electric field by a small particle and that is reflected by the pre-factor in Eq. (20). For a fractal small composite of many particles the situation differs essentially. Here the geometrical enhancement of the electric field is due to the focusing effect of fractal clustering reflected by the Mittag-Leffler function and it depends on the argument of the complex value of $p(\omega)$.

The exponential (geometric) enhancement takes place when $|p(\omega)| \gg 1$ and $\mathrm{Re}p(\omega) > 0$ as in Eq. (22). This condition is fulfilled for those frequencies ω that are in the vicinity of the SPR: $\mathrm{Re}p(\omega) = -2\varepsilon_d + \Delta$, where $\Delta \sim \varepsilon_2 \ll \varepsilon_d$.

We have to admit that the obtained expressions in the exponential forms are the upper bound of the electric field enhancement. The enhanced E_1 does not exceed of the order of 10^8(V/cm), otherwise the nonlinear effects become important that violates the linear quasi-static consideration. This restriction yields $r(\varepsilon_d/2\varepsilon_2) \leq 20$, which is a reasonable value for experimental realizations. Therefore, we have the light wavelength $\lambda \sim 10^{-4}$cm, fractal inhomogeneity size $l_0 \sim (10^{-6}$cm, and $\varepsilon_d/\varepsilon_2 \sim \omega\tau \sim 5 \div 15$, where ω is the optical frequency, while τ is the relaxation time. The latter value determines l_0, as well, which was introduced above as a minimum self-similarity size. Note that $\tau \leq \tau_s \equiv \frac{l_0}{v_F}$, where τ_s is the surface relaxation time, while v_F is the velocity on the Fermi surface (for free electrons). Therefore, from the condition $\omega\tau \gg 1$, one obtains $l_0 > \frac{v_f}{\omega} \sim 10^{-7}$cm.

5 Conclusion

It should be admitted that a traditional consideration of photocatalysis is based on the energy loss due to plasmon's decay that leads to generation of hot electrons and holes and suitable increase of oxidation-reduction processes. This effect is usually considered under investigation of macroscopic, electrochemical manifestation of plasmon resonance [3, 47, 48]. The main reason for this follows from the consideration of an individual nanoparticle that yields the maximum enhancement of the external field of the order of 10^2. Therefore, there is no any measurable chemical effects under such high frequency field ($\omega \sim 10^{15} sec^{-1}$) with the amplitude of the order of 10^2(V/cm), particularly under condition that this field exists only in the vicinity of the nanoparticle surface (on the distance of the order of the particle radius).

Following our consideration in Sec. 2, we were able to show that the manifestation of breakdowns of Stern double layer-capacitor due to the hot spots possible at the enhanced electric field of the order of $10^6 \div 10^7$(V/cm), and the observed effect is due to the anomalously strong electric field. Nevertheless, it should be stressed that these two different effects can simultaneously co-exist in the presence of the fractal self-similarity on the surface of nano-structured electrodes.

Therefore, the main goal of the paper was to develop an analytical method of calculation of the giant local enhancement of the optical electric field inside the fractal composite structure. It should be admitted that nano-structured noble-metal-dielectric composites are a standard object of nanoplasmonics. In our consideration this is a nano-structured electrode - electrolyte interface. In this sense, we speak about nanoplasmonic electrochemistry. Owing to the analytical expressions of enhanced electric field, one can analyze the experimental results in the field of photo and electrochemistry [7]. It is worth mentioning that all methods of the calculation of the enhancement of the electric field by fractal clusters used so for are different approximations [3].

We developed an analytical approach, for description of the wave propagation-localization in metal-dielectric nanostructures in the *quasi-static* limit. The method is based on fractional calculus and permits to obtain an analytical expressions for the electric field enhancement. This approach establishes a link between fractional geometry of the nanostructure and fractional integro-differentiation. An essential (geometrical) enhancement of the electric field is obtained

for the surface plasmon resonance at a certain relation between permittivities of the host and fractal metallic nanostructure, when $\mathrm{Re}\varepsilon_m(\omega) = -2\varepsilon_d$ with a suitable detuning.

Important part of the analysis is developing convolution integrals that makes it possible to treat the fractal structure. The initial Maxwell equation (6) is local, since $l_0/\lambda \ll 1$ and space heterogeneity is accounted locally by virtue of the characteristic function. An accurate treatment of the fractal boundaries and recasting the Maxwell equation in the form of the convolution integrals by accounting fractal properties of the composite, eventually, leads to the coarse graining equations, which already take into account the space heterogeneity and nonlocal nature of the electric field and polarized dipole charges inside the composite. Therefore, the heterogeneity, caused by the fractal geometry, is reflected by the convolution of the averaged fractal density and the electric field, according Eqs.(11) and (14). It is necessary to admit that this transform from "local" quasi-electrostatics to the nonlocal, which takes into account space dispersion of permittivity $\varepsilon(r)$ is mathematically justified and rigorous enough [42]. The obtained convolution integrals are averaged values, since the fractal density r^{D-3} is the averaged characteristics of the fractal structure, and, eventually, it determines the space dispersion of the permittivity $\varepsilon(r)$ of the mixture.

Summarizing, we have to admit that observation of macroscopic Maxwell's equations is related to averaging of microscopic equations [40]. This procedure for fractal composite media is not well defined so far, since, according fractal's definition, averaging over any finite volume depends on the size of this volume itself [43]. The main idea to overcome this obstacle is to refuse the local properties of equations and obtain nonlocal coarse graining Maxwell's equations, which are already averaged.

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6 Appendix A: Fractional calculus briefly

Extended reviews of fractional calculus can be found *e.g.*, in [19, 20, 18]. Fractional integration of the order of α is defined by the operator

$$ {}_aI_x^\alpha f(x) = \frac{1}{\Gamma(\alpha)} \int_a^x f(y)(x-y)^{\alpha-1} dy \,, $$

where $\alpha > 0,\ x > a$. Fractional derivation was developed as a generalization of integer order derivatives and is defined as the inverse operation to the fractional integral. Therefore, the fractional derivative is defined as the inverse operator to ${}_aI_x^\alpha$, namely ${}_aD_x^\alpha f(x) = {}_aI_x^{-\alpha} f(x)$ and ${}_aI_x^\alpha = {}_aD_x^{-\alpha}$. Its explicit form is

$$ {}_aD_x^\alpha f(x) = \frac{1}{\Gamma(-\alpha)} \int_a^x f(y)(x-y)^{-1-\alpha} dy \,. $$

For arbitrary $\alpha > 0$ this integral diverges, and, as a result of this, a regularization procedure is introduced with two alternative definitions of ${}_aD_x^\alpha$. For an integer n defined as $n-1 < \alpha < n$,

one obtains the Riemann-Liouville fractional derivative of the form

$$ {}_a^{RL}D_x^\alpha f(x) = \frac{d^n}{dx^n} {}_aI_x^{n-\alpha} f(x)\,, \tag{24} $$

and fractional derivative in the Caputo form

$$ {}_a^{C}D_x^\alpha f(x) = {}_aI_x^{n-\alpha} \frac{d^n}{dx^n} f(x)\,. \tag{25} $$

There is no constraint on the lower limit a. For example, when $a = 0$, one has ${}_0^{RL}D_x^\alpha x^\beta = \frac{x^{\beta-\alpha}\Gamma(\beta+1)}{\Gamma(\beta+1-\alpha)}$, $\alpha, \beta > 0$. This fractional derivation with the fixed low limit is also called the left fractional derivative. Another important property is $D^\alpha I^\beta = I^{\beta-\alpha}$, where other indexes are omitted for brevity's sake. A convolution rule for the Laplace transform for $0 < \alpha < 1$

$$ \mathcal{L}[I_x^\alpha f(x)] = s^{-\alpha}\tilde{f}(s) \tag{26} $$

is commonly used in fractional calculus as well.

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